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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/US91/07351</p> <p>(22) International Filing Date: 15 October 1991 (15.10.91)</p> <p>(30) Priority data: 599,284 18 October 1990 (18.10.90) US</p> <p>(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).</p> <p>(72) Inventors: LISS, Theodor, Arthur ; 105 Rockingham Drive, Wilmington, DE 19803 (US). RAO, Nandakumar, Sesha-giri ; 112 Brookrun Drive, Hockessin, DE 19707 (US).</p> <p>(74) Agents: FEENY, Charles, E. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>		<p>(81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL (European patent), NO, PL, RO, SD, SE (European patent), SN (OAPI patent), SU<sup>+</sup>, TD (OAPI patent), TG (OAPI patent).</p> <p><b>Published</b>  <i>With international search report.  Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p><b>(54) Title:</b> STAIN-RESISTANT SULFONATED AROMATIC POLYMERS</p> <p><b>(57) Abstract</b></p> <p>Stain-resistant, polyamide textile substrates treated with compositions comprising sulfonated aromatic polymers which contains between about 0.1 and 10 polymer units derived from one or more ethylenically unsaturated aromatic monomers per polymer unit derived from a sulfonated ethylenically unsaturated aromatic monomer, and processes for their preparation. The treated polyamide textile substrates possess stain-resistance but do not suffer from yellowing to the extent that some previously known materials have.</p>			

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- 1 -

TITLE

STAIN-RESISTANT SULFONATED AROMATIC POLYMERS

5 FIELD OF THE INVENTION

The present invention relates to polyamide textile substrates treated with stain-resistant compositions comprising sulfonated aromatic polymers, and processes for their preparation.

10

BACKGROUND OF THE INVENTION

Polyamide substrates, such as nylon carpeting, upholstery fabric and the like, are subject to staining by a variety of agents, e.g., foods and beverages. An especially troublesome staining agent is FD&C Red Dye No.40, commonly found in soft drink preparations. Different types of treatments have been proposed to deal with staining problems. For example, Liss et al., in U.S. Patent Application Serial No. 07/124,866, filed 23 November 1987, disclose stain-resistant synthetic polyamide textile substrates having deposited on them sulfonated phenol/formaldehyde polymeric condensation products. However, sulfonated phenol/formaldehyde condensation products are themselves subject to discoloration; commonly they turn yellow. W. H. Hemmpel in a March 19, 1982 article in America's Textiles, entitled Reversible Yellowing Not Finisher's Fault, attributes yellowing to exposure of a phenol-based finish to nitrogen oxides and/or ultra-violet radiation. To deal with the yellowing problem, the condensation products disclosed in the Liss et al. application have been modified by acylation or etherification of some of the phenolic hydroxyls. In a preferred embodiment, Liss et al. dissolve the modified condensation

- 2 -

products in a hydroxy-containing solvent, such as ethylene glycol, prior to their being applied to the textile substrate. On the other hand, in U.S. Patent 4,833,009, Marshall discloses removing color-forming 5 materials from sulfonated phenol/formaldehyde condensates by acidifying the condensate, applying heat, removing the resulting water-soluble phase and dissolving the insoluble phase in aqueous base prior to applying it to the textile substrate to make it 10 stain-resistant. In yet another approach, Fitzgerald et al., in European Patent Application No. 0329899 published 30 August 1989, disclose hydrolyzed vinyl-aromatic/maleic anhydride polymers having a number 15 average molecular weight between about 500 and 4000 as stain-resist agents, and polyamide textile substrates treated with those polymers. R.A. Weiss et. al. disclose in the Journal of Polymer Science, Polymer Chemistry Edition, Vol 23, 525-533 and 549-568 (1985) that whereas sulfonated ionomers (polymers containing 20 active groups such as sulfonic acid groups) had been prepared previously by sulfonation of the corresponding homopolymers, they had prepared copolymers of styrene and sodium styrene sulfonate by emulsion polymerization. Molecular weights obtained 25 were assumed to be high and similar to the molecular weights of the polymers formed by sulfonation of the homopolymers; e.g.  $M_n$  of 23,000 & 106,000.)

BRIEF SUMMARY OF THE INVENTION

30 The present invention provides polyamide textile substrates treated with sulfonated aromatic polymers so as to impart stain-resistance to the substrates, and methods for preparing the same. The treated polyamide textile substrates possess stain- 35

- 3 -

resistance but do not suffer from yellowing to the extent that some previously known materials have.

DETAILED DESCRIPTION OF THE INVENTION

5        The sulfonated polymers suitable for the purposes of this invention contain between about 0.1 and 10 polymer units derived from one or more ethylenically unsaturated aromatic monomers per polymer unit derived from a sulfonated ethylenically 10 unsaturated aromatic monomer. Polymers containing about 0.9 polymer unit derived from one or more ethylenically unsaturated aromatic monomers per polymer unit derived from a sulfonated ethylenically unsaturated aromatic monomer are most effective in 15 imparting stain-resistance to textile substrates.

20       A variety of aromatic monomers can be used for the purposes of this invention, e.g., styrene, alpha-methylstyrene, 4-methylstyrene, 4-methoxy-styrene, vinylbenzene-4-carboxylic acid, and the like, and mixtures of the same, with styrene being preferred. Likewise, there are various sulfonated monomers which can be used for the purpose of this invention. The sulfonated monomers usually are water-souble; for example, the alkali metal and 25 ammonium salts. Particular examples include sodium p-styrene sulfonate, sodium vinyl p-toluene sulfonate, ammonium p-styrene sulfonate. In addition, the foregoing ethylenically unsaturated aromatics can be sulfonated at the para and/or ortho positions and be 30 used for the purposes of this invention. An acrylic monomer can be added to either of the above-described two classes of monomers to give a terpolymer having useful dying properties, e.g. methacrylic acid, acrylic acid, itaconic acid, their lower alkyl esters 35 and the like.

- 4 -

The sulfonated polymers of this invention should have number average molecular weights in the range between about 500 and 7000, preferably between about 500 and 5000, most preferably 900 to 3000.

5 They are readily soluble, even at high concentrations, in water at 25-90°C and a pH of 2 or above; increasing dilution is needed at pHs below 2. They are also soluble in lower alcohols, such as methanol, ethylene glycol, propylene glycol, mixtures of ethylene and 10 hexylene glycols, and are somewhat soluble in acetic acid.

15 The polymers suitable for the purposes of this invention can be conveniently prepared by a variety of free radical-initiated polymerization reactions using methods known to the art for limiting the molecular weight of the products. One example is the benzoyl peroxide-initiated polymerization of styrene and sodium styrene sulfonate. Molecular weight control can be accomplished by the use of large 20 quantities of benzoyl peroxide, in the order of 10%, based on weight of monomers. Alternatively, chain transfer agents such as dodecyl mercaptan may be used with lesser amounts of benzoyl peroxide. Another preparative method is the solution polymerization of 25 the monomers using Vazo®67 2,2'-azobis(2-methylbutyronitrile) as an initiator and mercaptosuccinic acid as a chain transfer agent. In all of these methods, a convenient range of monomers plus initiator concentrations in the solvent is about 20 to 35%.

30 The sulfonated aromatic polymers of this invention not only cover the surface of the treated substrate, but particularly in the case of a fibrous substrate, the polymer at least in part permeates the fiber. The polymers can be used as such in treating 35 polyamide textile substrates. They can be applied to

- 5 -

dyed or undyed polyamide textile substrates. They can be applied to such substrates in the absence or presence of a polyfluoroorganic oil-, water-, and/or soil-repellent materials. In the alternative, such a 5 polyfluoroorganic material can be applied to the textile substrate before or after application of the sulfonated polymers of this invention thereto. The sulfonated polymers can be applied to textile substrates in a variety of ways, e.g. during 10 conventional beck and continuous dyeing procedures. The quantities of the polymers of this invention which are applied to the textile substrate are amounts effective in imparting stain-resistance to the substrate. The amounts can be varied widely; in 15 general, one can use between 0.5 and 5% by weight of them based on the weight of the textile substrate, usually 2% by weight or less. The polymers can be applied, as is common in the art, at pHs ranging between 4 and 5. However, more effective exhaust 20 deposition can be obtained at a pH as low as 2. When pH of 2 is used, the preferred level of application to the textile substrate is about 1.2% by weight of polymer, based on the weight of the textile substrate. More effective stainblocking is obtained if the 25 sulfonated polymers are applied to the textile substrate at higher temperatures. For example, at pH 2, 170°F is preferred. However, stain-resistance can be obtained at room temperature, or even at the temperature of cold tap water (10-15°C), if higher 30 levels of stainblockers are employed. The sulfonated polymers of this invention can also be applied in-place to polyamide carpeting which has already been installed in a dwelling place, office or other locale. They can be applied as a simple aqueous preparation or 35 in the form of aqueous shampoo preparation, with or

- 6 -

without one or more polyfluoro-organic oil-, water-, and/or soil-repellent materials. They may be applied at the levels described above, at temperatures described, and at a pH between about 1 and 12, 5 preferably between about 2 and 9.

The following Examples are illustrative of the invention. Unless otherwise indicated, all parts and percentages are by weight and temperatures in the Examples and Tests are in degrees Celsius. In the 10 examples that follow, stain-resistance and yellowing were measured by the techniques described below. Number average molecular weights are usually determined by vapor-phase osmometry. However, that method cannot be applied to compositions of this 15 invention because of the presence of glycols and other interfering lower molecular weight substances. In Example 1, number average molecular weights were approximated by gel permeation chromatography. On the other hand, gel permeation chromatography 20 determinations are difficult to run; consequently, no molecular weight determinations were made for the compositions of Examples 2-7.

Exhaust Application of Stain-Resists to Carpeting

25 Launder-0-Meter Method

Exhaust application of stain-resists to carpeting is carried out in a Launder-0-Meter automated dyeing machine. One carpet piece is contained in each of several (up to twenty) stainless 30 steel, screw-cap canisters. The canisters are held in a rack that rotates in a water bath whose temperature is automatically controlled for rate of heating, time at temperature and cooling. For a typical application bath, one uses a 20 to 1 liquor to goods ratio with 35 2.5 weight % of the stain-resistant composition. The

- 7 -

stain-resistant compositions can be applied at pH 2 or pH 5. At pH 2, an excess of sulfamic acid is used. At pH 5, an excess of ammonium sulfate is used, as well as 3g/L of magnesium sulfate and 1g/L of an alkyl 5 aryl sulfonate (Alkanol®ND) or a suitable leveling agent. After the bath is made up, a solution of the stain-resist composition is added to the Launder-o-Meter canister. The carpet sample to be treated is then placed in the canister, tufted side 10 out, the size of the carpet sample, relative to the size of the canister, being such that no portion of the sample touches another portion of the sample. The canisters are placed in the Launder-O-Meter and the water bath temperature is held at 110°F for 5 minutes. 15 The temperature of the water bath is then raised to the desired temperature for application of the stain-resist composition. For application at pH 2, the temperature of the water bath is raised to 170°F +/- 5°F, and for application at pH 5, the temperature 20 of the water bath is raised to 200°F +/- 5°F. After the bath water reaches the desired temperature, it is held there for 20 min. and then cooled to 100°F. The treated carpet sample is removed from the canister and rinsed by squeezing in deionized water at room 25 temperature. Three successive rinses in fresh deionized water are given, each rinse being at 40 volumes of water per volume of sample. The rinsed carpet sample is centrifuged to remove excess liquid and dried at 200°F. in a forced draft oven for 30 30 minutes. The dry carpet sample can then be tested by use of the tests described below.

Stain Test

The stain test is used to measure the extent 35 to which carpeting is stained by a commercial beverage

- 8 -

composition which contains FD&C Red Dye No. 40 (an acid dye). The staining liquid, if sold commercially as a liquid, is used as is. Usually the commercial product is in the form of a solid. In that event, the 5 beverage preparation, in dry, solid form, is dissolved in deionized water so as to provide 0.1 g of FD&C Red Dye No. 40 per liter of water. Sufficient wetting agent (Du Pont Merpol<sup>®</sup>SE liquid nonionic ethylene oxide condensate) is added to the dye solution to 10 provide 0.5 g of the wetting agent per liter of dye solution. Unless otherwise specified, the test sample is DuPont type 1150 Nylon 6,6 (white); Superba heatset, mock dyed level loop carpet, 3/8 inch pile height, 30 ounces per yard, 1/10 inch gauge, 10 15 stitches per inch, woven polypropylene primary backing. The test sample is wetted completely with water, and excess water is removed by centrifuging. The damp sample is placed tufted face down in a pan and covered with ten times its face weight of stain 20 fluid. Entrained air is expelled from the sample by squeezing or pressing. The sample is turned over and again the air is expelled. The sample is then returned to a face down position, and the pan is covered for storage for test period of 30 minutes. 25 The stored stain sample is rinsed in running cool water until no more stain is visually detectable in the rinse water. The rinsed sample is extracted in a centrifuge and dried at 200 degrees F. Staining is evaluated with the Minolta Chroma Meter tristimulus 30 color analyzer in the L\*A\*B Difference Mode with the target sample set for the unstained carpet. The "a" value is a measure of redness, with a value of 43 equal to that obtained on an untreated carpet. The stain-resistance of the resulting carpet sample is 35 visually determined by the amount of color left in

- 9 -

the stained area of the carpet sample according to the following scale:

- 5            5 = no staining
- 4            4 = slight staining
- 3            3 = noticeable staining
- 2            2 = considerable staining
- 1            1 = heavy staining.

UV YELLOWING TEST

10            The light-fastness of carpet samples treated with a stainblocker is determined by exposing the treated samples to UV light for 20 Hours. A sample piece of carpet that has been treated with a stain-blocker is placed in a box containing its hinged top a standard fluorescent fixture fitted with two forty watt lamps. Centered under the pair of lamps in the bottom of the box is a sliding tray having a 3 inch x 40 inch recess for holding carpet specimens. The depth of the recess is such that the distance from the carpet face to the plane defined by the lamp surfaces is 1 inch. The current to the lamp is controlled by a timer so that a twenty-hour exposure can be obtained automatically. After the twenty-hour exposure, the reflectance of CIE White Light Source C from the carpet is compared with the reflectance from an unexposed sample and the CIELAB delta "b" noted. Delta "b" is a measure of the yellow component of white light. A Minolta Chroma Meter model CR-110 reflectance meter is used to make the measurements and to calculate delta "b" automatically from stored data on the unexposed sample. The value of "b" is reported as the measure of yellowing with increasing positive values of "b" corresponding to increased degrees of yellowing.

- 10 -

The Minolta Chroma Meter is used in the Hunter L\*a\*b color-deviation measuring mode [Richard Hunter, "Photoelectric Colorimetry with Three Filters," J. Opt. Soc. Am., 32, 509-538 (1942)]. In the measuring mode, the instrument measures the color differences between a "target" color, whose tristimulus color values have been entered into the microprocessor as a reference, and the sample color presented to the measuring head of the instrument. In examining carpet samples for yellowing and for FD&C Red Dye No. 40 staining, the "target" color entered is that of the carpet before yellowing or staining. The color reflectance of the yellowed or stained carpet is then measured with the instrument and reported as:

\*E, the total color difference, \*L, the lightness value,  
\*a, the redness value, if positive, or greenness, if negative, and  
\*b, the yellowness value, if positive, or blueness, if negative.

Example 1

Ethylene glycol, 800 g, was added to a 2 liter flask, heated to 70°C with a nitrogen sparge and held at that temperature for 1 hour. It was cooled to 25°C and sodium styrene sulfonate, 150 g (0.73 mol), was added with agitation in about 5 minutes. Agitation was continued until a solution was obtained, about 45 minutes. A solution of styrene, 50 g (0.48 mol), in hexylene glycol, 200 g, was added over 15 minutes, and the reaction mixture was allowed to warm to 65-70°. Benzoyl peroxide, 40.0 g (0.165 mol), was added in 3 portions, each portion 1/2 hour apart. The temperature was allowed to rise to about 85° during these additions. The mass was maintained

- 11 -

at 80° for 8 hours. A yellow to amber solution of the polymer was obtained, solids = 19%, residual monomer 1%, and molecular weight ranging from 800 to 7000 by gel permeation chromatography.

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Example 2

Example 1 was repeated with 91.8 g (0.44 mol), of sodium styrene sulfonate and 108.6 (1.04 mol), of styrene. The reaction proceeded in 10 fashion similar to that of Example 1.

Example 3

Ethylene glycol, 98.0 g, was added to a 250 ml flask and heated to 70° with a nitrogen sparge 15 and held at that temperature with agitation for 1 hour. It was cooled to 25° and sodium styrene sulfonate, 8.3 g (0.04 mol), and itaconic acid, 5.2 g (0.04 mol), was added with agitation in about 5 minutes. Agitation was continued until solution was 20 complete, about 30 minutes. A solution of styrene, 6.3 g (0.06 mol), in hexylene glycol, 25 g, was added over 15 minutes and the mixture was allowed to heat to 65-70°. Benzoyl peroxide, 4.8 g (0.02 mol), was added in one portion. A 6° heat rise was noted. The mass 25 was maintained at 80° for 8 hours. An amber solution of polymer was obtained, solids = 13%.

Example 4

A mixture of ethylene glycol, 170 g, and 30 hexylene glycol, 43 g, was heated with a nitrogen sparge and agitation to 70° and held for 1 hour. It was cooled to 25°. Vinylbenzene-4-carboxylic acid, 29.6 g (0.2 mol), and sodium styrene sulfonate, 30.9 g (0.15 mol), were added to the solvent mixture to yield 35 a clear solution. The mass was heated to 70° and

- 12 -

benzoyl peroxide, 23.2 g (0.1 mol), was added. A 6° heat rise was observed. The reaction mass was held at 80° for 8 hours. A clear yellow polymer solution was obtained, solids = 18.7%.

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Example 5

Example 4 was repeated using vinylbenzyl chloride, 22.9 g (0.2 mol), instead of the vinyl-benzyl-4-carboxylic acid. A dark brown polymer solution was obtained, solids = 17.9%.

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Example 6

Ethylene glycol, 73 g, was heated to 70° with a nitrogen sparge and held at that temperature for 1 hour with agitation. It was cooled to 25° and sodium styrene sulfonate, 40.6 g (0.2 mol), and dodecyl mercaptan, 3.6 g (0.016 mol), were added. A solution of styrene, 31.5 g (0.3 mol), in hexylene glycol, 73 g, was added over 5 minutes and the reaction mixture was allowed to warm to 65-70°.

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Benzoyl peroxide, 230 g (0.095 mol), was added in one portion. A 6° heat rise was noted. The mass was held at 80° for 8 hours. A clear yellow viscous solution of polymer was obtained, solids = 38%.

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- 13 -

TABLE 1

	<u>Example</u>					
	1	2	3	4	5	6
5						
	Initial					
	Discoloration	2.4	2.3	2.3	2.6	3.5
	Staining	7.1	8.7	6.2	12.7	14.8
	UV yellowing	1.0	1.0	1.3	1.6	2.3
10						

Example 7

Sodium styrene sulfonate, 37.5 g (0.18 mol), in 200 g of acetic acid was heated to 70° with agitation under nitrogen at atmospheric pressure.

15 Sufficient water, 38.0 mls., to dissolve the sodium styrene sulfonate was added. There were then added in turn a solution of 12.5 g (0.12 mol) of styrene in 50 g of acetic acid, 7.5 g (0.05 mol) of mercapto-succinic acid and 9.1 g (0.05 mol) of Vazo® 67 [2,2'-azobis-(2-methylbutyronitrile)]. The temperature was raised to 80° and the mass was held overnight at 80° to yield a pale yellow product solution.

20 Nylon film treated with a solution of this product showed no staining with FD&C Red Dye No. 40.

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- 14 -

CLAIMS

1. A polyamide textile substrate treated with an effective amount of a composition capable of 5 imparting stain-resistance to it comprising a sulfonated aromatic polymer having a number average molecular weight in the range of between about 500 and 7000 which contains between about 0.1 and 10 polymer units derived from one or more ethylenically 10 unsaturated aromatic monomers per polymer unit derived from a sulfonated ethylenically unsaturated aromatic monomer.

2. The polyamide substrate of Claim 1 15 wherein said polymer contains between about 0.9 and about 3 polymer units derived from one or more ethylenically unsaturated aromatic monomers per polymer unit derived from a sulfonated ethylenically unsaturated aromatic monomer.

20 3. The polyamide substrate of Claim 2 wherein said ethylenically unsaturated aromatic monomer is styrene, alpha-methyl-styrene, 4-methyl-styrene, or 4-methoxystyrene, vinylbenzene-4- 25 carboxylic acid, or mixtures of the same.

30 4. The polyamide substrate of Claim 3 wherein said ethylenically unsaturated aromatic monomer is styrene.

5. The polyamide substrate of Claim 2 wherein said sulfonated ethylenically unsaturated aromatic monomer is sodium styrene sulfonate.

- 15 -

6. The polyamide substrate of Claim 1  
wherein said sulfonated aromatic polymer has a  
molecular weight (number average) in the range between  
about 500 and 5,000.

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7. The polyamide substrate of Claim 6  
wherein said sulfonated aromatic polymer has a  
molecular weight (number average) in the range between  
about 900 and 3,000.

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8. A process for imparting stain-resistance  
to a textile substrate which comprises applying to  
said substrate an effective amount of a composition  
comprising a sulfonated aromatic polymer having a  
15 number average molecular weight in the range between  
about 500 and 7000 which contains between about 0.1  
and 9 polymer units derived from one or more  
ethylenically unsaturated aromatic monomers per  
polymer unit derived from a sulfonated ethylenically  
20 unsaturated aromatic monomer.

9. The process of Claim 8 wherein said  
sulfonated aromatic monomer contains between about 0.4  
and 3 polymer units derived from one or more  
25 ethylenically unsaturated aromatic monomers per  
polymer unit derived from a sulfonated ethylenically  
unsaturated aromatic monomer.

10. The process of Claim 9 wherein said  
30 ethylenically unsaturated aromatic monomer is styrene,  
alpha-methylstyrene, 4-methylstyrene, or 4-methoxy-  
styrene, vinylbenzene-4-carboxylic acid, or mixtures  
of the same.

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- 16 -

11. The process of Claim 10 wherein said ethylenically unsaturated aromatic monomer is styrene.

5 12. The process of Claim 11 wherein said sulfonated ethylenically unsaturated aromatic monomer is sodium styrene sulfonate or sodium vinyltoluene sulfonate.

10 13. The process of Claim 8 wherein said sulfonated aromatic polymer has a molecular weight (number average) in the range between about 500 and 5,000.

15 14. The process of Claim 13 wherein said sulfonated aromatic polymer has a molecular weight (number average) in the range between about 900 and 3,000.

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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/07351

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)<sup>6</sup>According to International Patent Classification (IPC) or to both National Classification and IPC  
Int.Cl. 5 D06M15/233

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System	Classification Symbols
Int.Cl. 5	D06M ; D06P

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

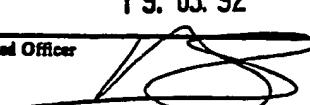
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	FR,A,1 443 521 (HOECHST AG.) 16 May 1966 see claims; example 3 ---	1-14
X	EP,A,0 333 500 (ALLIED COLLOIDS LIMITED) 20 September 1989 see page 3, line 35 - line 38; claims; example 3 ---	1-14
A	US,A,2 700 001 (COHEN ET AL.) 18 January 1955 see the whole document ---	1-14
A	EP,A,0 329 899 (E.I. DU PONT DE NEMOURS AND COMPANY) 30 August 1989 cited in the application see the whole document ---	1-14
E	EP,A,0 456 390 (ALLIED COLLOIDS LIMITED) 13 November 1991 see the whole document ---	1-14

<sup>10</sup> Special categories of cited documents :<sup>10</sup>

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## IV. CERTIFICATION

Date of the Actual Completion of the International Search 2 13 MARCH 1992	Date of Mailing of this International Search Report 19. 03. 92
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer BLAS V. 

**ANNEX TO THE INTERNATIONAL SEARCH REPORT**  
**ON INTERNATIONAL PATENT APPLICATION NO. US 9107351**  
**SA 53722**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 13/03/92

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US-A-2700001		None		
EP-A-0329899	30-08-89	AU-A- JP-A- US-A-	2708988 2138365 5001004	15-06-89 28-05-90 19-03-91
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